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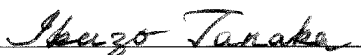
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Japanese Patent Application No. 2002-216840

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Date: July 10, 2008

  
Ikuzo Tanaka

## SPECIFICATION

### Title of the Invention

#### PISTON RING

#### Claims:

1. A piston ring for an internal combustion engine comprising a coating film comprising a heat-resistant material and a solid lubricant dispersed therein on at least one side surface, said heat-resistant material comprising at least one of a polyamideimide-silicon dioxide hybrid material and a polyimide-silicon dioxide hybrid material.
2. The piston ring according to claim 1, wherein said solid lubricant comprises an inorganic compound, an inorganic simple substance or a fluororesin, and has an average particle size of 0.1 to 20  $\mu\text{m}$ .
3. The piston ring according to claim 2, wherein said solid lubricant comprises at least one material selected from the group consisting of molybdenum disulfide, tungsten disulfide, boron nitride, graphite, polytetrafluoroethylene resins and tetrafluoroethylene-perfluoroalkyl vinyl ether copolymer resins.
4. The piston ring according to any one of claims 1 to 3, wherein the content of said solid lubricant in the entire film is 5 to 80% by mass.
5. The piston ring according to any one of claims 1 to 4, wherein said piston ring comprises a nitrided layer having a thickness of 3 to 120  $\mu\text{m}$  formed on a substrate of said piston ring.

## **DETAILED DESCRIPTION OF THE INVENTION**

[0001]

### **Field of the Invention**

The present invention relates to a piston ring for internal combustion engines having a resin film with a low friction coefficient.

[0002]

### **Prior Art**

In internal combustion engines, pistons are put into reciprocating motion by explosive combustion of fuels in combustion chambers, whereby piston rings repeatedly collide with piston grooves. In gasoline engines, areas around a top ring are heated to approximately 250°C by the explosive combustion. Further, the temperature of the areas is higher in the case of diesel engines. When a piston made of an aluminum alloy is pounded with a piston ring at such a high temperature, a surface of the piston groove is fatigued, broken and peeled off, whereby aluminum fragments fall out. The aluminum fragments or the aluminum alloy in clean surfaces provided by the breakage adhere a side surface of the piston ring. This phenomenon is referred to as "aluminum adhesion." As the aluminum adhesion proceeds, the piston ring is fixed onto the piston groove, thereby losing gas sealability. Thus, "blow-by," in which high-pressure combustion gas flows from a combustion chamber into a crankcase, is caused to reduce the engine output. Further, the piston ring also loses oil sealability, so that oil consumption is increased.

[0003]

Proposals have been made to prevent the fixation of the top piston ring onto the piston groove due to the aluminum adhesion are methods in which the piston ring is not allowed to come in contact with the base

material of the aluminum alloy directly.

[0004]

The proposals made regarding the piston side include a method disclosed in JP 63-170546 A, in which the piston groove is subjected to an anodization treatment (alumite treatment) and a lubricating material is filled in pores of the anodized surface. A hard oxide film mainly composed of aluminum oxide is formed on the piston groove by the alumite treatment, whereby the falling of the aluminum fragments is prevented and the aluminum adhesion to the piston ring is not caused. However, the alumite treatment of the piston is disadvantageous in high costs.

[0005]

The proposals made regarding the piston ring side include methods disclosed in JP-UM 60-82552 A and JP 62-233458 A. In the method disclosed in JP-UM 60-82552 A, a heat-resistant, wear-resistant resin film, which is composed of a solid lubricant such as molybdenum disulfide, graphite, carbon and boron nitride dispersed in a tetrafluoroethylene resin or an oxybenzoyl polyester resin, is formed on a phosphate salt film or a triiron tetroxide film provided on a side surface of the piston ring. In the method disclosed in JP 62-233458 A, a film, in which a solid lubricant such as molybdenum disulfide is dispersed in a heat-resistant resin such as an epoxy resin, a phenol resin, a polyamide resin and a polyimide resin, is formed on a side surface of the piston ring. The content of the solid lubricant of molybdenum disulfide is desirably 60 to 95% by mass, and the friction coefficient between the piston groove and the side surface of the piston ring is reduced by cleavage of the solid lubricant. However, though the solid lubricant decreases the wear of the piston, the wear cannot be completely prevented because of the softness of the heat-resistant resin used as a base

material for the film. Thus, the piston rings provided by the methods are insufficient in durability though these methods are effective for preventing the aluminum adhesion at the initial stage. Particularly, in high output engines, the resin films wear in a relatively short period by the high temperature and pounding, and the base material in the side surface come into contact with the aluminum alloy in the piston groove, thereby causing the aluminum adhesion.

[0006]

JP 9-184079 A has disclosed a film for improving the durability of the piston ring. This film has a base of a manganese phosphate layer with a larger roughness, the molybdenum disulfide particles having a particle size of 1 to 2  $\mu\text{m}$  are dispersed and accumulated on the concave portions of the manganese phosphate layer, whereby the film can prevent the aluminum adhesion for a long period of time. However, though the durability is improved, the film is less effective for preventing the aluminum adhesion because the convex portions of the manganese phosphate layer are in contact with aluminum early.

[0007]

To prevent the aluminum adhesion, polyamideimide (PAI) has been mainly used as a binder for the films. Though the polyamideimide is an excellent resin with heat resistance and softness, it is a polar polymer to be high in hygroscopicity. Therefore, when the polyamideimide touches moisture provided by the combustion of a hydrocarbon-based fuel at a high temperature, it is likely to absorb the moisture. The moisture absorption turns the polyamideimide remarkably poor in mechanical strength, softness, and adhesiveness to the substrate, so that the films using the polyamideimide as a binder are easily broken or peeled off, and worn out when pounded and

slid at a high temperature in the engines. The same is equally true for polyimide (PI). As just described, the conventional resin films can be insufficient in the durability because of the moisture absorption of the binder.

[0008]

Further, the polyamideimide and the polyimide are organic polymer compounds, easily oxidized or decomposed at a high temperature. Thus, the polymer compounds are disadvantageously poor in the durability in engines with high combustion temperature, and it is likely that they cannot be applied to high-top piston rings for use at an increased temperature, intended for adaptation to high output engines and strict exhaust gas regulations.

[0009]

Recently, much attention has been paid to organic-inorganic hybrid materials, which have advantages of both organic and inorganic compounds. JP 2001-240670 A has disclosed a polyamideimide-silicon dioxide hybrid material that has improved mechanical strength and heat resistance while maintaining softness and extensibility of the polyamideimide. This polyamideimide-silicon dioxide hybrid material can be produced by grafting an alkoxysilane onto a polyamideimide having a carboxyl group (-COOH) or an acid anhydride group at the end, and by heat-treating the resultant silane-modified polyamideimide resin. This polyamideimide-silicon dioxide hybrid material has a moisture absorption coefficient lower than that of a simple polyamideimide, as described in Polymer Preprint, Japan, Vol. 49, No. 14 (2000). Further, a polyimide-silicon dioxide hybrid material, which is extremely higher in breaking strength and tensile elasticity than a simple polyimide, is described in Plastics Age, Mar. 2002, 130-132 and Polymer

Preprint, Japan, Vol. 50, No. 11 (2001). The polyimide-silicon dioxide hybrid material can be produced by grafting methoxysilane onto side chains of polyamic acid composed of pyromellitic acid and oxadiazaniline, and by heat-treating the resultant silane-modified polyamic acid.

[0010]

#### **Problems to be solved by the Invention**

Accordingly, an object of the present invention is to provide a piston ring having a solid lubricant-dispersed coating film on a side surface thereof, the solid lubricant-dispersed coating film comprising a binder having high heat resistance, high mechanical strength and low hygroscopicity to effectively prevent aluminum adhesion over a long period of time.

[0011]

#### **Means for solving the Problems**

As a result of intense research in view of the above object, the inventors have found that by replacing polyamideimide or polyimide that has been used as a heat-resistant material in conventional resin coating films, with a heat-resistant material composed of at least one of a polyamideimide-silicon dioxide hybrid material and a polyimide-silicon dioxide hybrid material, it is possible to provide a resin coating film for piston rings with improved heat resistance, mechanical strength and adhesiveness to the piston ring substrate, and with reduced hygroscopicity and wear rate, thereby preventing the adhesion of aluminum to the side surface of the piston ring for a long period of time. The present invention has been completed based on this finding.

[0012]

Thus, a piston ring for an internal combustion engine according to the present invention comprises a coating film comprising a heat-resistant

material and a solid lubricant dispersed therein on at least one side surface, the heat-resistant material comprising at least one of a polyamideimide-silicon dioxide hybrid material and a polyimide-silicon dioxide hybrid material.

[0013]

The solid lubricant preferably comprises an inorganic compound, an inorganic simple substance or a fluororesin, and preferably has an average particle size of 0.1 to 20  $\mu\text{m}$ . More specifically, the solid lubricant preferably comprises at least one material selected from the group consisting of molybdenum disulfide, tungsten disulfide, boron nitride, graphite, polytetrafluoroethylene resins and tetrafluoroethylene-perfluoroalkyl vinyl ether copolymer resins. Further, the content of the solid lubricant in the entire coating film is preferably 5 to 80% by mass.

[0014]

A nitrided layer having a thickness of 3 to 120  $\mu\text{m}$  may be formed on a substrate of the piston ring.

[0015]

### **Best Mode for carrying out the Invention**

[1] Substrate of piston ring

Although there are no particular restrictions in a substrate of the piston ring of the present invention, the substrate is preferably made of a material having excellent durability. Examples of preferred materials for the substrate include steels, martensite stainless steels, austenite stainless steels, high-grade cast irons, titanium alloys, etc. The substrate of the piston ring may be subjected to a treatment of nitriding, phosphatization, plating, etc., beforehand.

[0016]



[2] Resin coating film

The resin coating film of the piston ring contains at least one of a polyamideimide-silicon dioxide hybrid material and a polyimide-silicon dioxide hybrid material as the heat-resistant material, and further contains solid lubricant particles highly dispersed in the heat-resistant material.

[0017]

(1) Heat-resistant material

The heat-resistant material comprises at least one of the polyamideimide-silicon dioxide hybrid material (hybrid material of polyamideimide and silicon dioxide) and a polyimide-silicon dioxide hybrid material (hybrid material of polyimide and silicon dioxide) to compose the resin coating film as a binder. The term “hybrid material” means a so-called organic-inorganic hybrid material provided by compounding or complexing an organic material with a metal oxide. The organic-inorganic hybrid material is not a mixture of an organic compound and an inorganic compound, but a product of synthesis where they are compounded or complexed at the molecular level in a synthesis step. Examples of the hybrid materials include those prepared by heat-treating silane-modified resins and oxidizing silanes into silicon dioxide. The silane-modified resin may be obtained by a reaction of polyamideimide and/or polyimide with a partial condensation product of glycidyl ether group-containing alkoxysilane. The coating film using the organic-inorganic hybrid material as the heat-resistant material is low in hygroscopicity, and high in heat resistance, mechanical strength, adhesiveness to the substrate and flexibility, thereby excellent in durability. To obtain the coating film with more excellent durability, the content of silicon dioxide to the entire hybrid material is preferably 0.2 to 30% by mass. When the content of silicon dioxide is less

than 0.2% by mass, the hybrid material is less effective for reducing the hygroscopicity and for increasing the mechanical strength. When the content of silicon dioxide is more than 30% by mass, the coating film is so brittle that it easily peels off by pounding.

[0018]

(2) Solid lubricant

It is preferable to use an inorganic lubricant and a fluororesin alone or in combination as the solid lubricant. The inorganic lubricant is cleaved in the sliding operation to reduce the friction coefficient of the coating film. Thus, the coating film containing the inorganic lubricant has high wear resistance and can prevent the aluminum adhesion for a long period. Examples of such inorganic lubricants include inorganic compounds such as molybdenum disulfide, graphite, tungsten disulfide and boron nitride, and inorganic simple substances such as graphite.

[0019]

The fluororesin is less reactive with each other and with other substances, thereby having a low friction coefficient and functions as the solid lubricant. Examples of the preferred fluororesins include straight-chain polymers of tetrafluoroethylene ( $\text{CF}_2=\text{CF}_2$ ), such as polytetrafluoroethylene resins (PTFE), tetrafluoroethylene-perfluoroalkyl vinyl ether copolymer resins (PFA), etc. Among the fluororesins, the polytetrafluoroethylene resins (PTFE) are particularly excellent in the solid lubrication function and has particularly low friction coefficient. The fluororesins have spreading properties to be easily spread on the sliding surface by pounding and sliding. Thus, the coating films containing the fluororesins have a high wear resistance. In particular, in a case where the coating film has a high fluororesin-content, the coating film is entirely

covered with a layer provided by spreading the fluororesin, so that the coating film becomes lower in the friction coefficient and higher in the durability to maintain the aluminum adhesion-preventing effect over a longer period of time.

[0020]

The average particle size of the solid lubricant is preferably 0.1 to 20  $\mu\text{m}$ , more preferably 0.1 to 10  $\mu\text{m}$ . When the average particle size is less than 0.1  $\mu\text{m}$ , the solid lubricant is poor in the solid lubrication function. When the average particle size is more than 20  $\mu\text{m}$ , the solid lubricant is easily detached from the coating film, and, accordingly, the coating film is worn out relatively rapidly.

[0021]

### (3) Others

A resin hardener, a reinforcing material such as antimony trioxide, etc. may be appropriately added to the resin coating for the piston ring of the present invention.

[0022]

## [3] Production of piston ring

### (1) Pretreatment

The substrate of the piston ring is preferably subjected to a pretreatment such as a nitriding treatment and a surfactant treatment. In the nitriding treatment, a hard nitrided layer is formed on the surface of the substrate. The nitrided layer improves the wear resistance of the peripheral face of the piston ring, and increases scuff resistance of the piston ring to the sliding mate cylinder made of an aluminum alloy. The method for the nitriding treatment may be gas nitriding, ion nitriding, salt bath nitriding, sulphonitriding, etc. The thickness of the nitrided layer is preferably 3 to

120  $\mu\text{m}$ . When the thickness is less than 3  $\mu\text{m}$ , the wear resistance of the piston ring is insufficient. When the thickness is more than 120  $\mu\text{m}$ , the piston ring is easily broken.

[0023]

After the nitriding treatment, oils on the surfaces of the substrate may be removed by a degreasing treatment using alkali, hydrocarbon, etc. After the degreasing treatment, the resultant substrate may be subjected to a pretreatment such as acid cleaning and phosphate treatment, if necessary.

[0024]

(2) Preparation of hybrid material

The hybrid material may be prepared by a known method. The silane-modified resins can be preferably prepared by methods described in JP 2001-240670 A, *Plastics Age*, Mar. 2002, 130-132, *Polymer Preprint*, Japan, Vol. 50, No. 11 (2001), etc. For example, a partial condensation product of a glycidyl ether group-containing alkoxysilane is prepared by a dealcoholization reaction between a partial condensation product of tetramethoxysilane and a glycide (or glycidol), and then reacted with a polyamideimide and/or polyimide having a carboxyl group and/or an acid anhydride group at the end, to obtain a silane-modified polyamideimide and/or a silane-modified polyimide resin.

[0025]

These silane-modified polyamideimide and the silane-modified polyimide may act as a silane coupling agent. Because the silane uniformly exists in the polyamideimide molecules in proper quantity, the solid lubricant-dispersed coating can firmly adhere to the piston ring substrate without particular pretreatments.

[0026]

(3) Preparation of coating liquid

A solid lubricant-dispersed varnish (coating liquid) may be obtained by mixing the solid lubricant or the solid lubricant dispersion with a varnish, which is prepared by dissolving the polyamideimide-silicon dioxide hybrid material and/or the polyimide-silicon dioxide hybrid material in a solvent mainly composed of *N*-methyl-2-pyrrolidinone, etc. The amount of the added solid lubricant is preferably 5 to 80% by mass, more preferably 30 to 70% by mass, based on the mass of the coating film after drying. When the amount is less than 5% by mass, the friction coefficient of the coating film cannot be sufficiently reduced, whereby the coating film is easily worn. When the amount is more than 80% by mass, the heat-resistant material cannot sufficiently hold the solid lubricant, so that the solid lubricant is easily fallen off, and as a result, the coating film is poor in the wear resistance.

[0027]

(4) Formation of resin coating film

The obtained coating liquid may be applied to at least one of the upper and lower surface of the piston ring. To more effectively prevent the aluminum adhesion due to collision between the piston groove and the piston ring, the coating liquid is preferably applied to both the side surfaces, more preferably the entire surfaces, of piston ring. From the viewpoints of improving the resistance against the aluminum adhesion, the coating liquid may be applied to only portions to be particularly easily worn. For example, the coating liquid may be applied only to the lower surface of the piston ring, which is rapidly worn by pounding generally.

[0028]

The coating liquid is preferably applied by a known method such as

spray coating, dip coating, spin coating, roll coating, electrostatic coating, printing, etc. The spray coating methods are more preferable from the viewpoints of preventing mottles and improving the efficiency of solvent removal. Further, the printing methods such as screen-printing are more preferable from the viewpoints of high application efficiency and low environmental pollution.

[0029]

After the application, the coating film may be formed by a hardening treatment. The hardening conditions depend on the heat-resistant material. In the case of forming the coating film using the polyamideimide-silicon dioxide hybrid material as the heat-resistant material, the hardening treatment is preferably carried out at 170 to 300°C for 30 to 120 minutes. When the hardening temperature is lower than 170°C, the hardening reaction cannot proceed sufficiently, whereby the desired mechanical strength and moisture absorption resistance due to the heat-resistant material are not obtained. When the hardening temperature is higher than 300°C, the formed coating film is degraded by oxidative decomposition. Further, when the hardening time is less than 30 minutes, the hardening reaction cannot proceed sufficiently, whereby the desired mechanical strength and moisture absorption resistance due to the heat-resistant material are not obtained. When the hardening time is more than 120 minutes, the hardening reaction does not proceed anymore, thereby resulting in waste of time and energy.

[0030]

The thickness of the resin coating film is preferably 3 to 40  $\mu\text{m}$ , more preferably 5 to 15  $\mu\text{m}$ . When the thickness is less than 3  $\mu\text{m}$ , the coating has insufficient wear resistance. When the thickness is more than

40  $\mu\text{m}$ , it is difficult to fit the piston ring in the piston groove.

[0031]

As described above, the piston ring effective for preventing the aluminum adhesion can be obtained by using at least one heat-resistant resin selected from the polyamideimide-silicon dioxide hybrid material and the polyimide-silicon dioxide hybrid material as a binder, and by forming a coating film containing the solid lubricant dispersed in the heat-resistant resin on at least one side surface of the piston ring.

[0032]

The present invention will be explained in more detail referring to Examples below without intention of restricting the present invention thereto.

[0033]

#### Example 1

##### (1) Pretreatment

Surfaces of a top ring substrate made of a martensite stainless steel were nitrided by a gas nitriding method, and degreased by a commercially-available, alkaline degreasing liquid. Then, the substrate was washed with water and sufficiently dried.

[0034]

##### (2) Preparation of coating liquid

Molybdenum disulfide particles having an average particle size of 5  $\mu\text{m}$  and graphite particles having an average particle size of 4  $\mu\text{m}$  as solid lubricants were added to Compoceran H901 available from Arakawa Chemical Industries, Ltd. in amounts of 30% and 10% by mass, respectively, on a solid basis, and sufficiently stirred to prepare a coating liquid containing uniformly dispersed solid lubricants. Compoceran H901 was a varnish of a silane-modified polyamideimide resin as a heat-resistant

material in a mixed solvent of *N*-methyl-2-pyrrolidone and xylene (mass ratio = 80:20), the concentration of each of polyamideimide and silicon dioxide being 30% by mass. The coating liquid was diluted with a mixture of *N*-methyl-2-pyrrolidone and xylene, and stirred to prepare a spray coating liquid.

[0035]

(3) Formation of resin coating film

The obtained coating liquid was applied to one side surface of the pretreated substrate by a spray method, and hardened at 250°C for 1 hour, to form a resin coating film comprising the polyamideimide-silicon dioxide hybrid material and the solid lubricants dispersed therein. The composition of the coating film and the thickness of the coating film after the hardening treatment are shown in Table 1.

[0036]

Example 2

Using a varnish (Compoceran H800 available from Arakawa Chemical Industries, Ltd.) of a silane-modified polyimide resin in a mixed solvent of *N*-methyl-2-pyrrolidone and xylene (mass ratio = 80:20), the concentration of each of polyimide and silicon dioxide being 18% by mass, a coating liquid was applied to one side surface of a top ring substrate and hardened in the same manner as in Example 1 except for changing the hardening temperature to 300°C, to form a resin coating film comprising a polyimide-silicon dioxide hybrid material and solid lubricants dispersed therein. The composition of the coating film and the thickness of the coating film after the hardening treatment are shown in Table 1.

[0037]

Example 3



Using a varnish containing the silane-modified polyamideimide resin in Example 1 and the silane-modified polyimide resin in Example 2 in a mixed solvent of *N*-methyl-2-pyrrolidone and xylene (mass ratio = 80:20), at a mass ratio of the polyamideimide-silicon dioxide hybrid material to the polyimide-silicon dioxide hybrid material of 1:1 after the hardening treatment, a coating liquid was applied to one side surface of a top ring substrate and hardened in the same manner as in Example 1 except for changing the hardening temperature to 300°C, to form a resin coating film comprising the polyamideimide-silicon dioxide hybrid material, the polyimide-silicon dioxide hybrid material, and solid lubricants dispersed in the hybrid materials. The composition of the coating film and the thickness of the hardened coating film are shown in Table 1.

[0038]

#### Comparative Example 1

##### (1) Pretreatment

Surfaces of a top ring substrate made of a martensite stainless steel were nitrided by a gas nitriding method, and degreased by a commercially-available, alkaline degreasing liquid. Then, the substrate was washed with water, sufficiently dried, and washed with trichloroethylene.

[0039]

##### (2) Formation of resin coating film

A solid lubricant-dispersed resin liquid (Defric HMB-2 available from Kawamura Kenkyusho) containing a solid lubricant mainly composed of molybdenum disulfide and graphite dispersed in polyamideimide was sprayed to one side surface of a top ring substrate, and hardened at 190°C for 1 hour to form a resin coating film. The composition of the coating film and the thickness of the hardened coating film are shown in Table 1.

[0040]

Comparative Example 2

A resin coating film was formed on one side surface of a top ring substrate in the same manner as in Example 1 except for using polyamideimide as a heat-resistant material. The composition of the coating film and the thickness of the hardened coating film are shown in Table 1.

[0041]

Comparative Example 3

A resin coating film was formed on one side surface of a top ring substrate in the same manner as in Example 3 except for using polyimide as a heat-resistant material. The composition of the coating film and the thickness of the hardened coating film are shown in Table 1.

[0042]

Comparative Example 4

A resin coating film was formed on one side surface of a top ring substrate in the same manner as in Example 1 except for using a mixture of polyamideimide and polyimide (mass ratio = 1:1) as a heat-resistant material, and for changing the hardening temperature to 300°C. The composition of the coating film and the thickness of the hardened coating film are shown in Table 1.

[0043]

[Table 1]

	Heat-resistant material	Mass ratio of lubricants to solid contents of film (% by mass)		Film thickness ( $\mu\text{m}$ )	
		MoS <sub>2</sub>	Graphite	A	B
Example 1	PAI-SiO <sub>2</sub>	30	10	10	9
Example 2	PI-SiO <sub>2</sub>	30	10	10	10
Example 3	PAI-SiO <sub>2</sub> + PI-SiO <sub>2</sub> (Mass ratio: 1:1)	30	10	11	10
Comparative Example 1	PAI	Unknown	Unknown	10	8
Comparative Example 2	PAI	30	10	9	9
Comparative Example 3	PI	30	10	9	10
Comparative Example 4	PAI + PI (Mass ratio: 1:1)	30	10	10	10

Note: Films of A were subjected to aluminum adhesion test immediately after the film formation, and films of B were subjected to aluminum adhesion test after moisture absorption test.

[0044]

#### Moisture absorption test

Each top ring used in Examples 1 to 3 and Comparative Examples 1 to 4 was stored in a thermostatic chamber at 25°C in a relative humidity of 30% for 24 hours before the formation of a coating film, and weighed by an electronic balance to obtain a weight  $m_1$ . After the formation of a coating film, each top ring was stored in a thermostatic chamber at 25°C in a relative humidity of 30% for 24 hours, and weighed by an electronic balance to obtain a weight  $m_2$ . Each coated top ring was further stored in a thermostatic chamber at 50°C in a relative humidity of 90% for 24 hours, and weighed by an electronic balance to obtain a weight  $m_3$ . A moisture

absorption coefficient  $a$  of each resin coating film was calculated by the following equation:  $a = 100 \times (m_3 - m_2) / (m_2 - m_1)$ .

[0045]

#### Adhesiveness test

Using the same materials as used for coating top rings in Examples 1 to 3 and Comparative Examples 1 to 4, coating films were formed on each flat plate of 30 mm  $\times$  30 mm  $\times$  1 mm by the same treatment as in Examples 1 to 3 and Comparative Examples 1 to 4. Each coated plate was boiled for 24 hours, sufficiently dried at 100°C, left to stand at room temperature for 24 hours. Thereafter, each coated plate was subjected to a cross-cut tape test to evaluate the adhesiveness of the coating.

[0046]

#### Aluminum adhesion test

The top rings produced in Examples 1 to 3 and Comparative Examples 1 to 4 were subjected to aluminum adhesion test using the adhesion-testing machine shown in Fig. 1. In the aluminum adhesion test, a thermocouple 5 was inserted into a piston 2, the piston 2 was heated by a heater 1 controlled by a temperature controller 4, the piston 2 was put into reciprocating motion up and down whereby a side surface of a top ring 3 having a resin film was pounded, and the top ring 3 was rotated at a constant rate and slid on the piston 2. The piston was made of a material of JIS AC8A (T6) and was in a disk shape with the diameter of 100 mm, and the top ring had the outer diameter of 75 mm. The top ring was rotated at the circumferential rotational speed of 3.3 mm/s, the pressure of the pounding was 0.57 MPa, the pounding cycle was 3.3 Hz, and lubricating oils were not used.

[0047]

# Results of moisture absorption test

The results of the moisture absorption test of the top rings shown in Table 1 according to Examples 1 to 3 and Comparative Examples 1 to 4 are shown in Table 2.

[0048]

The films using the polyamideimide-silicon dioxide hybrid material, the polyimide-silicon dioxide hybrid material or the combination thereof as the binder were clearly lower in the moisture absorption coefficient than the films using the polyamideimide, the polyimide or the combination thereof as the binder.

[0049]

[Table 2]

Top ring	Moisture absorption coefficient (%)
Example 1	0.83
Example 2	0.78
Example 3	0.77
Comparative Example 1	1.64
Comparative Example 2	1.75
Comparative Example 3	1.55
Comparative Example 4	1.58

[0050]

## Results of adhesiveness test

The results of the adhesiveness test of the plates having the films according to Examples 1 to 3 and Comparative Examples 1 to 4 are shown in Table 3.

[0051]

[Table 3]

Film	Number of peeled portions (out of 100 portions)
Example 1	0
Example 2	0
Example 3	0
Comparative Example 1	27
Comparative Example 2	15
Comparative Example 3	30
Comparative Example 4	24

[0052]

Results of aluminum adhesion test

Fig. 2 shows the number of collision until the aluminum adhesion occurred in each top ring in Examples 1 to 3 and Comparative Examples 1 to 4. As shown in Fig. 2, the top rings of Examples 1 to 3 having the solid lubricant-dispersed coatings containing the PAI-SiO<sub>2</sub> hybrid material, the PI-SiO<sub>2</sub> hybrid material or their combination as a binder were clearly higher in resistance to the aluminum adhesion than those of Comparative Examples 1 to 4 with the coatings containing polyamideimide + polyimide as a binder.

[0053]

Further, in the case of the top rings in Comparative Examples 1 to 4, the pounding numbers causing the aluminum adhesion (aluminum adhesion resistance) measured before the moisture absorption were reduced to 1/2 to 2/3 by the moisture absorption. On the contrary, in the case of the top rings in Examples 1 to 4, the aluminum adhesion resistance was hardly reduced by the moisture absorption. Thus, it can be said that the top rings of Examples 1 to 4 are more excellent in water resistance than the top rings

of Comparative Examples 1 to 4.

[0054]

### **Effects of the invention**

Formed on at least one side surface of the piston ring of the present invention is a solid lubricant-dispersed coating comprising a polyamideimide-silicon dioxide hybrid material, a polyimide-silicon dioxide hybrid material or the combination thereof as a binder, which has high mechanical strength, excellent softness and low hygroscopicity. Therefore, the solid lubricant-dispersed coating film of the present invention can more effectively prevent or retard the aluminum adhesion between a ring groove and a top ring, as compared with the conventional coating films for preventing the aluminum adhesion

### **Brief Description of the Drawings**

[Fig. 1] Fig. 1 is a schematic sectional view showing an adhesion testing machine; and

[Fig. 2] Fig. 2 is a graph showing number of pounding to cause aluminum adhesion onto each top ring having a resin film.

### **Explanation of Symbols and Numerals**

- 1 . . . Heater,
- 2 . . . Piston,
- 3 . . . Top ring (Piston Ring),
- 4 . . . Temperature Controller, and
- 5 . . . Thermocouple.

**Abstract**

**Problems to be solved:**

5 To provide a piston ring having a solid lubricant-dispersed coating film on a side surface thereof, the solid lubricant-dispersed coating film comprising a binder having high heat resistance, high mechanical strength and low hygroscopicity to effectively prevent aluminum adhesion over a long period of time.

**Solution:**

10 A piston ring for an internal combustion engine comprising a coating film comprising a heat-resistant material and a solid lubricant dispersed therein on at least one side surface, the heat-resistant material comprising at least one of a polyamideimide-silicon dioxide hybrid material and a polyimide-silicon dioxide hybrid material.

15

**Selected Drawings:**

None



# Drawings

Fig. 1

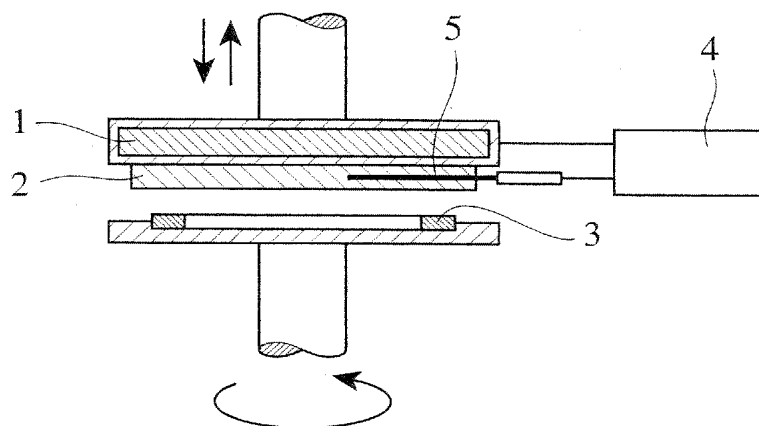


Fig. 2

